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Effect of dose rate, temperature and impurity content on the radiation damage in the electron irradiated NaCl crystals

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Abstract

The dependencies of void formation and radiolytic sodium accumulation on the irradiation dose, dose rate, temperature and impurity content are analyzed within a framework of a theoretical model, which is based on a new mechanism of dislocation climb. The mechanism involves the production of V_F centers (self-trapped hole neighboring a cation vacancy) as a result of the absorption of excess H centers at dislocation lines. Voids are shown to arise due to the reaction between F and V_F centers at the surface of halogen bubbles. All reactions involved in the evolution of extended defects are controlled by the difference between the absorption of H centers and F centers. This difference is determined by the material specific parameters responsible for the bias factors of extended defects and by the mean concentration of point defects. The latter depends on the temperature and dose rate as described in the present paper. Impurities can facilitate or suppress radiation damage formation depending on their effect on the nucleation of extended defects under irradiation. This is demonstrated by comparing theoretical results obtained for dose dependence of colloid volume fraction at different dislocation densities with experimental data obtained in crystals doped with different impurities. © 2000 Elsevier Science B.V. All rights reserved.

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Keywords: Radiation damage; Alkali halides; Voids; Bubbles; Colloids

1. Experimental results

Pure and doped synthetic NaCl crystals have been irradiated with 0.5 MeV electrons from a linear accelerator up to fluences 6×10^{18} electrons/

cm² (about 300 Grad or 30 displacements per anion) at dose rate 240 Mrad/h at fixed different temperatures between 30°C and 150°C. Scanning electron microscopy (SEM) has been carried out to study the void formation in heavily irradiated samples. Fig. 1 shows that void sizes, concentrations and shapes are very different for different impurities.

The volume fraction of the metallic Na precipitates ('colloids') has been deduced from the latent heat of melting (LHM) of sodium with a

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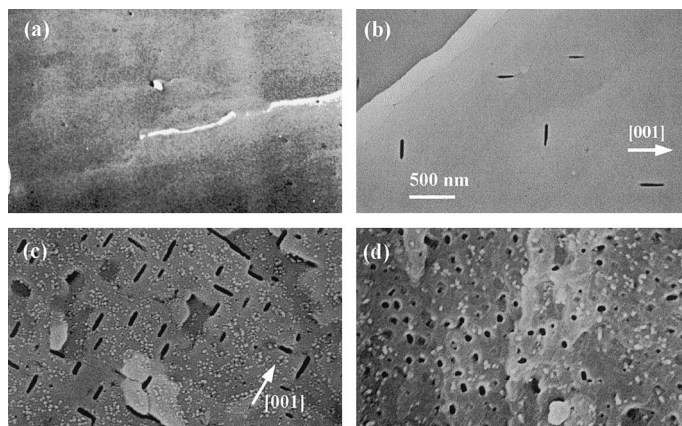


Fig. 1. SEM micrographs showing vacancy voids in pure and doped NaCl samples irradiated with 0.5 MeV electrons at 100°C, 240 Mrad/h to a dose of 300 Grad: (a) pure NaCl with a few small spherical voids; latent heat of melting (LHM) of metallic Na is 0.6 J/g; (b) low density of 'penny-shaped' voids in NaCl:Ba (0.05%); LHM of metallic Na is 0.64 J/g; (c) high density of 'penny-shaped' voids in NaCl:K (0.1%); LHM of metallic Na is 3.6 J/g; (d) high density of large spherical voids in NaCl:KBF₄ (0.03%); LHM of Na is 5.6 J/g.

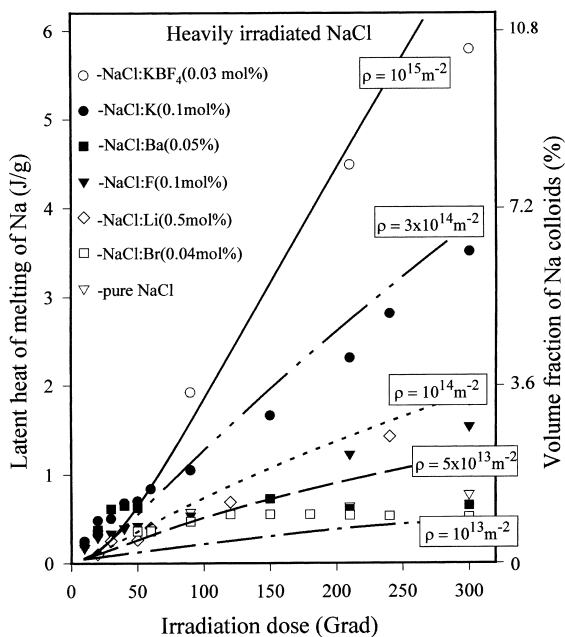


Fig. 2. Comparison of experimental data on dose dependence of colloid volume fraction (proportional to the LHM of Na) in crystals doped with different impurities and irradiated at 100°C, 240 Mrad/h with theoretical results obtained for different dislocation densities assuming bubble number density $N_B = 3 \times 10^{23} \text{ m}^{-3}$.

Perkin Elmer DSC-7 differential scanning calorimeter. Impurity effects on the colloid volume fraction have been investigated by comparing the results for pure, synthetic NaCl crystals and those doped with K, Ba, Li, F, Br and KBF₄ at different concentrations ranging from 0.03 to 0.5 mol% (Fig. 2). It is evident that some impurities strongly facilitate the colloid growth, which then does not show any sign of saturation predicted by previous models (see Section 2).

2. Theory

In the alkali halides, irradiation with electrons of moderate energies ($\sim 1 \text{ MeV}$) or gamma rays causes electronic excitations that produce Frenkel pairs only in the halide sub-lattice, which are called H and F centers. The H center is an interstitial halide ion with a trapped hole, and an F center is the vacancy in the halide sub-lattice with a trapped electron. From our results it follows that large *vacancy voids* (up to hundreds of nm in size) are formed (Fig. 1) together with metallic Na precipitates ('colloids') (Fig. 2). The void formation requires agglomeration of both cation and anion vacancies, which can not be explained by the conventional Jain and Lidiard model [1]. The lat-

ter describes the colloid growth in alkali halides as a result of the *dislocation bias* for H centers, which leads to an excess of F centers precipitating in colloids. However, the mechanism of dislocation climb [2] used in the Jain and Lidiard model, requires two H centers and leaves behind a molecular center, i.e. halogen molecule trapped in a stoichiometric vacancy pair (two adjacent vacancies, one in the cation and one in the anion sublattice). Thus, only dispersed molecular centers and metal colloids can be formed according to the Jain and Lidiard model. To explain our experimental results we use an original model of radiation damage formation in alkali halides [3] which is based on a new mechanism of dislocation climb.

2.1. New mechanism of dislocation climb

When an H center approaches a dislocation, it is assumed to displace a lattice cation and form with this ion a stoichiometric interstitial pair (needed for the dislocation climb) leaving behind a hole trapped next to a cation vacancy (see Fig. 3). The latter is known as the V_F center, which is a mobile ‘antimorph’ of the F center (electron trapped in an anion vacancy). This reaction is more straightforward than the one proposed by Hobbs et al. [2], and which is used in the Jain and Lidiard model. The new reaction requires only one H center as compared to two H centers meeting at the dislocation core, according to the mechanism [2].

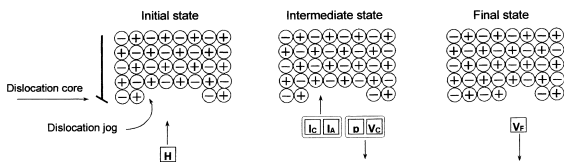


Fig. 3. Production of the V_F center as a result of absorption of an H center by an edge dislocation. When an H center approaches the dislocation, it displaces a lattice cation and forms with it a stoichiometric interstitial pair, $i_A + i_C$, where i_A and i_C are the anion and cation interstitials, respectively, and an H center is $i_A + p$ (i.e. an interstitial anion plus a hole, p). A cation vacancy, V_C , and a hole, are produced in the same reaction. The interstitial pair joins a dislocation jog leaving behind the hole trapped at the cation vacancy, that is a V_F center.

But what is more important is that the V_F center produced in this reaction is an ‘antimorph’ of the F center so that their mutual recombination would result in production of a stoichiometric vacancy pair. Such a recombination is expected to take place first of all at halogen bubble surfaces since coherent colloids are assumed to be transparent for V_F centers and do not trap them. Indeed, the V_F center is a defect in the cation sublattice that is not damaged by coherent colloids. An important consideration is that the production of V_F centers by dislocations requires an excess of incoming H centers over F centers, since the latter induce a back reaction (Fig. 3). Similarly, the production of vacancy pairs at the bubble surface requires an excess of incoming F centers over H centers. This means that all reactions involved in the production and absorption of V_F centers at extended defects are controlled by the biases for absorption of H centers or F centers.

2.2. Radiation-induced evolution of extended defects

An edge dislocation is biased towards absorption of H centers due to stronger elastic interaction with them as compared to F centers. The dislocation bias is determined by the ratio of relaxation volumes associated with H and F centers, Ω_H/Ω_F , and is given by [3]

$$\delta_d = \ln \left(\frac{\Omega_H}{|\Omega_F|} \right) / \ln \left(\frac{2}{L_H k_H} \right), \quad (1)$$

$$L_H \equiv \frac{\mu b(1 + \nu)}{3\pi kT(1 - \nu)} \Omega_H,$$

where b is the host lattice spacing, μ is the shear modulus of the matrix, ν is the Poisson ratio, k_H is the square root of the total sink strength of all extended defects for H centers, and kT has its usual meaning. So dislocations are an effective source of V_F centers under irradiation, as well as of extra F centers, which are left in the matrix after absorption of extra H centers.

Agglomeration of F centers gives rise to formation of metallic colloids, which are expected to be coherent with the host matrix as long as they are small. In this coherent state, there exists a misfit, ε , which is equal to the difference between

the lattice constants of the colloid and that of the host lattice. Positive (or negative) misfit means that colloid is under compressive (or tensile) stress having the radial component σ_e , which influences its bias towards absorption of H centers:

$$\sigma_e \equiv -\frac{3K_C\varepsilon}{1 + 3K_C/4\mu}, \quad (2)$$

where K_C is the colloid bulk modulus. In NaCl, coherent sodium colloids have a negative misfit of about 6% and, hence, a large positive misfit bias, which in the linear approximation in σ_e/μ is given by [3]

$$\delta_e = \alpha^d(\sigma_e/\mu), \quad (3)$$

where α^d is the constant corresponding to the elastic-diffusion anisotropy interaction between point defects and colloids [3].

The growth (or shrinkage) rate of colloid of a radius R_C is given by the difference of F and H center influxes, or equivalently, by the difference between the mean bias, $\bar{\delta}$, and the colloid bias, δ_C , that depends on its size, R_C , and structure/aggregation state,

$$\frac{dR_C}{dt} = \frac{1}{R_C} \left[Z_F^C D_F \bar{c}_F (\bar{\delta} - \delta_C) - Z_F^C D_F c_F^{(e)} \exp \left\{ \frac{2\gamma\omega}{kTR_C} \right\} \right], \quad (4)$$

$$\delta_C = \alpha_c^{\text{im}} b / R_C + \delta_e, \quad (5)$$

where D_F is the F center diffusivity and \bar{c}_F is their radiation-induced concentration that is determined by the rate equations, and the last term in (4) corresponds to the thermal dissolution of colloids, which is proportional to the thermal equilibrium concentration of F centers, $c_F^{(e)} = \exp(-E_F^f/kT)$, and the colloid surface energy, γ . E_F^f is the formation energy of F center, α_c^{im} is the constant of the image interaction between point defects and colloids, which determines radiation-induced dissolution of colloids [3].

The nucleation of halogen bubbles can start as a result of the recombination of V_F centers, the rate of which is proportional to the square of V_F center concentration. When several H centers

come to such a center they combine to form a halogen bubble which ‘digs its own hole’ in the lattice by punching out a perfect self-interstitial loop (SIA-loop) [4]. At later stages of radiolysis, the bubble size increases, and surplus F centers start to arrive at the bubble surface and recombine with V_F centers producing stoichiometric vacancy pairs that would increase the volume available for the halogen precipitate and so decrease the pressure below the threshold level for loop punching. After that, the bubble pressure is determined both by the number of halogen molecules and the number of vacancy pairs associated with it via the equation of state. Accordingly, the bubble evolution takes place in the two-dimensional phase space of the number of halogen molecules, n_{Gas} , and the number of vacancy pairs in it, n_{Vac} , as it is schematically shown in Fig. 4. Below some critical number of halogen molecules, $n_{\text{Gas}}^* \approx 10^2$, a bubble is forced to occupy a stable position along the curve in the ‘valley’ where its bias is equal to the mean bias of the system, and both components of the bubble growth rate are zero. A gradual de-

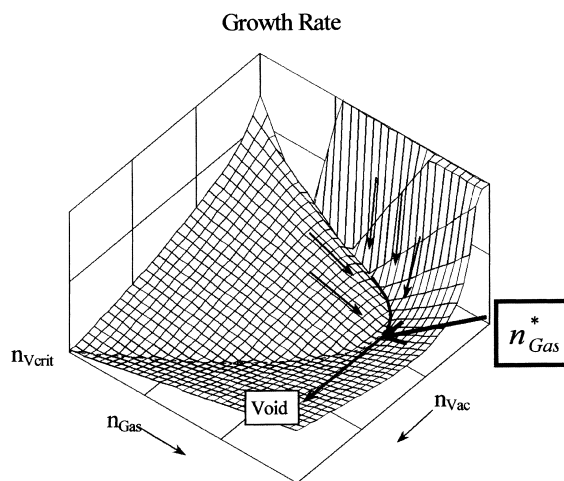


Fig. 4. The evolution path of bubbles resulting in their conversion to voids [3]. Below the critical number of halogen molecules, n_{Gas}^* , the bubbles move slowly along the valley, which provide the only stable path towards the point where the critical number of halogen molecules is reached. After the point is reached, the number of vacancies starts to increase, while the number of gas molecules stays constant. n_{Vacrit} is the critical number of vacancies required for growth of an empty void ($n_{\text{Gas}} = 0$).

crease of the mean bias, which is due to the colloid growth, makes the bubbles move adiabatically along the curve until they reach a critical point, beyond which n_{vac} would increase inexorably while n_{Gas} remains constant. Thus a conversion of bubbles to voids would take place after some threshold irradiation dose is reached, as it is shown in Fig. 5. It can be seen that volume fractions of colloids, bubbles and voids differ insignificantly (Fig. 5(d)) while their number densities and sizes differ drastically (Fig. 5(b,c)). Only a small fraction of bubbles is converted to voids that have no misfit bias and grow very fast as compared to colloids. According to our calculations of the dose dependence of radiation damage, the void dimensions can exceed the mean distance, first, between bubbles and then between colloids (R_{expl} in Fig. 5(c)) resulting in their collisions with voids. Collisions with bubbles fill the voids with gas, and subsequent collisions with colloids bring the halogen gas and

metal to a back reaction inside the voids, as described in more details in a companion paper [5].

2.3. Temperature/dose rate dependence of the colloid production

The temperature dependence of the colloid evolution is governed by two parameters, namely, by the migration and formation energies of F centers. The former determines bulk recombination of F and H centers, which decreases with increasing temperature until it becomes negligible as compared to recombination at extended defects. The formation energy determines concentration of thermal F centers, which rapidly increases with increasing temperature and must be taken into account at high irradiation temperatures (or low dose rates). The steady-state colloid volume growth rate is roughly proportional to the difference $D_{\text{F}}\bar{c}_{\text{F}} - D_{\text{F}}c_{\text{F}}^{(e)}$, which increases with temper-

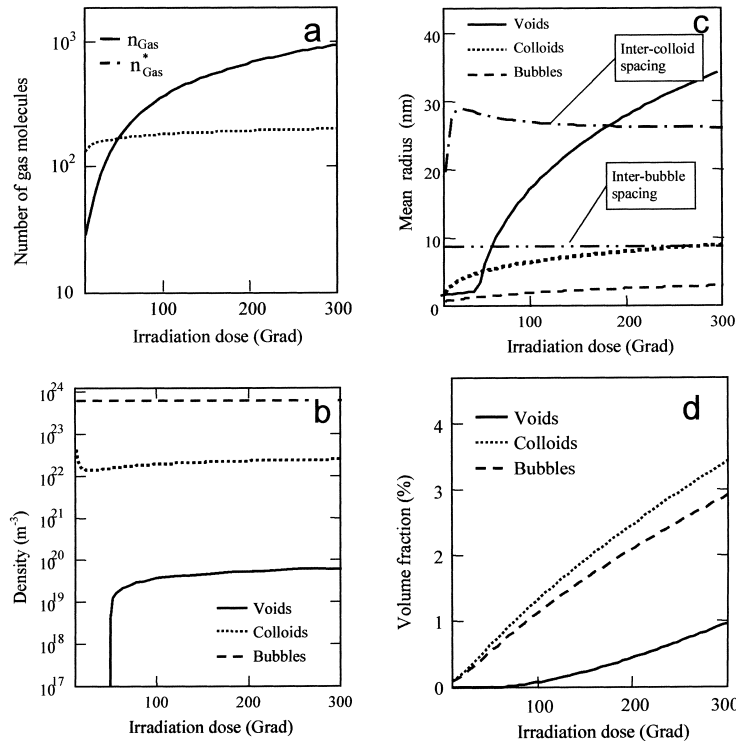


Fig. 5. Calculated dose dependence of the mean number of halogen molecules per bubble, n_{Gas} (a), number densities (b), mean radii (c) and volume fractions (d) of extended defects in NaCl irradiated at 100°C, 240 Mrad/h assuming dislocation density $\rho_{\text{d}} = 10614 \text{ m}^{-2}$ and bubble number density $N_{\text{B}} = 3 \times 10^{23} \text{ m}^{-3}$.

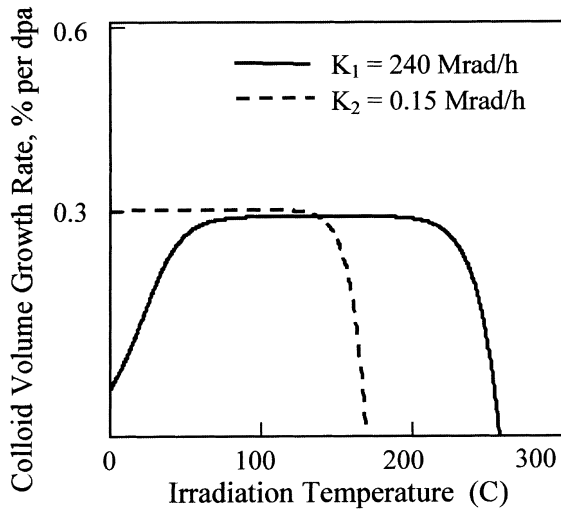


Fig. 6. Steady-state growth rate of colloid volume fraction at different dose rates, corresponding to the laboratory irradiation (K_1) and irradiation in the nuclear waste repository (K_2). The upper temperature cutoff is determined by the sum of the F center formation and migration energies and by the dose rate.

ature in the region of bulk recombination and decreases in the region of thermal point defect domination. In the intermediate region, where both bulk recombination of point defects and their thermal production are negligible, the growth rate per dpa reaches its maximum value, which is independent on temperature and dose rate and is

determined only by the sink strengths. The result is shown in Fig. 6 both for the laboratory dose rate and for that assumed to model the radwaste repository irradiation. In both cases, we can see the usual bell shape temperature dependence shifting along the temperature axis with changing dose rate. The observed temperature and dose rate dependence of colloid production can be more complex due to unspecified colloid nucleation mechanisms, which need further investigation.

3. Comparison of experimental results with theory

From our experimental data (Fig. 2) it is evident that some impurities can strongly facilitate the colloid growth, which then does not show any signs of saturation predicted by previous models (see e.g. [6]). There are many ways in which impurities can affect the formation of radiation damage. One of the most obvious ways is that impurity atoms can be nucleation centers for extended defects under irradiation, if they trap certain types of mobile point defects. If, for example, they can trap H centers, that would probably increase the dislocation density, ρ , and the bubble number density, N_B , which enter our model as free parameters (colloid and void number densities are calculated) (see Table 1). The impurity-induced

Table 1
Material parameters of NaCl and Na colloids used in calculations

Parameter	Value
Diffusion coefficient of H-centers, D_H , m^2/s	$10^{-6} \exp(-0.1 \text{ eV}/kT)$
Diffusion coefficient of F-centers, D_F , m^2/s	$10^{-6} \exp(-0.7 \text{ eV}/kT)$
Diffusion coefficient of V_F centers, D_V , m^2/s	$10^{-6} \exp(-0.69 \text{ eV}/kT)$
Formation energy of F centers, E_F^f , eV	1.0
F–H recombination rate constant, β_r , m^{-2}	10^{20}
Matrix shear modulus, μ , GPa	12
Colloid bulk modulus, K_C , GPa	6.3
Interface energy of coherent colloid, γ , J/m ²	0.01
Atomic volume of the host lattice, ω , m ⁻³	4.4×10^{-29}
Ratio of relaxation volumes of H and F centers, $\Omega_H/ \Omega_F $	2.4
Colloid misfit, ε	0.068
Elastic-diffusion anisotropy interaction constant, α^d	4
'Image' interaction constant for coherent colloids, α_c^{im}	0.41
Dislocation bias, δ_d , Eq. (1)	0.38
Misfit bias, δ_e , Eq. (3)	0.29

difference in dislocation density can be one of the reasons for the different responses of doped materials to irradiation. This is demonstrated in Fig. 2 by comparing theoretical results obtained for dose dependence of colloid volume fraction at different dislocation densities with experimental data obtained in crystals doped with different impurities.

Acknowledgements

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